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THE SYNTHESIS OF BORON CARBIDE FILAMENTS

2nd QUARTERLY REPORT

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by

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Space Sciences Laboratory
Missile and Space Division
General Electric Company
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SUMMARY

A

As presented in the First Quarterly Report, B_4C whiskers were produced by vapor deposition and identified. At that time the decision was made to pursue the pure vapor method rather than the dynamic flow method since the former method was more successful. The pure vapor method has been utilized throughout this phase of the program. By increasing the surface area of the B_4C refractory the B_4C vapor in the system has been increased and this has led to a 50-fold increase in the length of B_4C whiskers. Growth studies have indicated that more strict control of the operating parameters is required, therefore it was necessary to make revisions in the furnace design. Also a continuing search for effective catalysts to increase the growth rate of whiskers is progressing. Further studies on the morphology, orientation, crystal structure, etc., of B_4C whiskers produced are continuing and will be reported upon. Preliminary strength characteristics of the B_4C whiskers produced to date are being measured and will be presented.

Future work includes the continued effort on growth studies utilizing redesigned equipment. A major effort will be directed towards measuring the physical properties of the B_4C whiskers. It is felt that this most important phase be documented as fully as possible so that the future of the program can be assessed. Preliminary studies leading to the fabrication of test composites will also be made and include such parameters as bonding, coatings, choice of matrix, etc.

AUTHOR

I. INTRODUCTION

The purpose of this program is to synthesize Boron Carbide whiskers, to ascertain their mechanical properties, and to utilize such whiskers in metal-based composites. The impetus for this work is based on the exceptionally high strength of such "perfect" crystals. A description and discussion of such properties and the possible incorporation of such crystals in composites has been described in a previous report[1]. The successful utilization of super strong crystals can lead to a new class of high strength, high temperature composites capable of increasing by an order of magnitude, the present capability of our strongest materials.

The program thus far has emphasized growth studies leading to an adequate supply of B_4C whiskers for testing and composite fabrication. Concurrent with the growth studies, the morphology, crystal structure, orientation, etc., is being documented. The acquisition of a Tecam® Micro-tensile Tester* has enabled us to begin an evaluation of the mechanical properties of B_4C whiskers. A description of this instrument together with preliminary strength results will be included in this progress report.

*Designed by D. M Marsh, Tube Investments Lab., Cambridge, England.

II. EXPERIMENTAL PROCEDURES AND RESULTS

The study thus far has developed into a three-phased project. The growth phase has been directed toward producing adequate supplies of whiskers for the other study phases and for the ultimate goal of fabricating and testing composites. Optimization of process variables in terms of quality and physical characteristics of the B_4C whiskers is also a major part of the growth phase. Strength studies are a very important phase of this program. The strength characteristics of B_4C whiskers as a function of such variables as whisker orientation, diameter, temperature, etc. will be necessary in order to predict composite strengths and to eventually fabricate strong useful composites. The structure studies supplement both the growth and strength phases and also add to our basic scientific knowledge of fibrous composites.

A. GROWTH OF B_4C WHISKERS

Emphasis during this quarter has been placed on producing boron carbide whiskers by the pure vapor method of deposition (i.e. by the vaporization of boron carbide at approximately 1900°C and recondensing the vapor as boron carbide whiskers at a lower temperature). This work has been done in the large vacuum deposition furnace described in the first quarterly report[1].

The effect of temperature on the growth process appears to be critical. The original vaporization crucible (2.5 cm diameter) provided approximately 5 cm^2 of vaporization area. A new boron carbide "crucible" was constructed from A. T. J. graphite in the form of a "Lazy Susan", that is, six concentric trays of diminishing diameter were supported on a central rod of graphite (Figure 1). This provides a crucible area of 80 cm^2 for the vaporization process. Micron lengths of boron carbide whiskers were obtained in using the original crucible, while whisker lengths of about one millimeter were obtained in using the new crucible. A second fifteen tray "Lazy Susan" (Figure 2) with a tray area of approximately 180 cm^2 was constructed which filled

Figure 1. Photograph of Initial "Lazy Susan" - Actual Size

most of the vaporization section of the furnace. Whiskers with lengths greater than 5 mm have now been obtained. The optimum furnace conditions at present are: 5 hour duration furnace heats, with a temperature of 1900°C in the vaporization area and approximately 1700°C temperature in the whisker deposition area. Physically the "Lazy Susan" is supported 1-1/2" above the furnace bottom allowing the top two trays of boron carbide to extend into the chimney section of the deposition tube. Figure 3 shows whiskers on the edge of the adapter ring (refer to Figure 5 of the First Quarterly Report[1]) of a deposition mandrel. This type of whisker formation extends approximately four centimeters into the chimney of the deposition mandrel.

An adapter is presently under construction which will provide for the stacking of the two small vapor deposition furnaces (one such furnace was

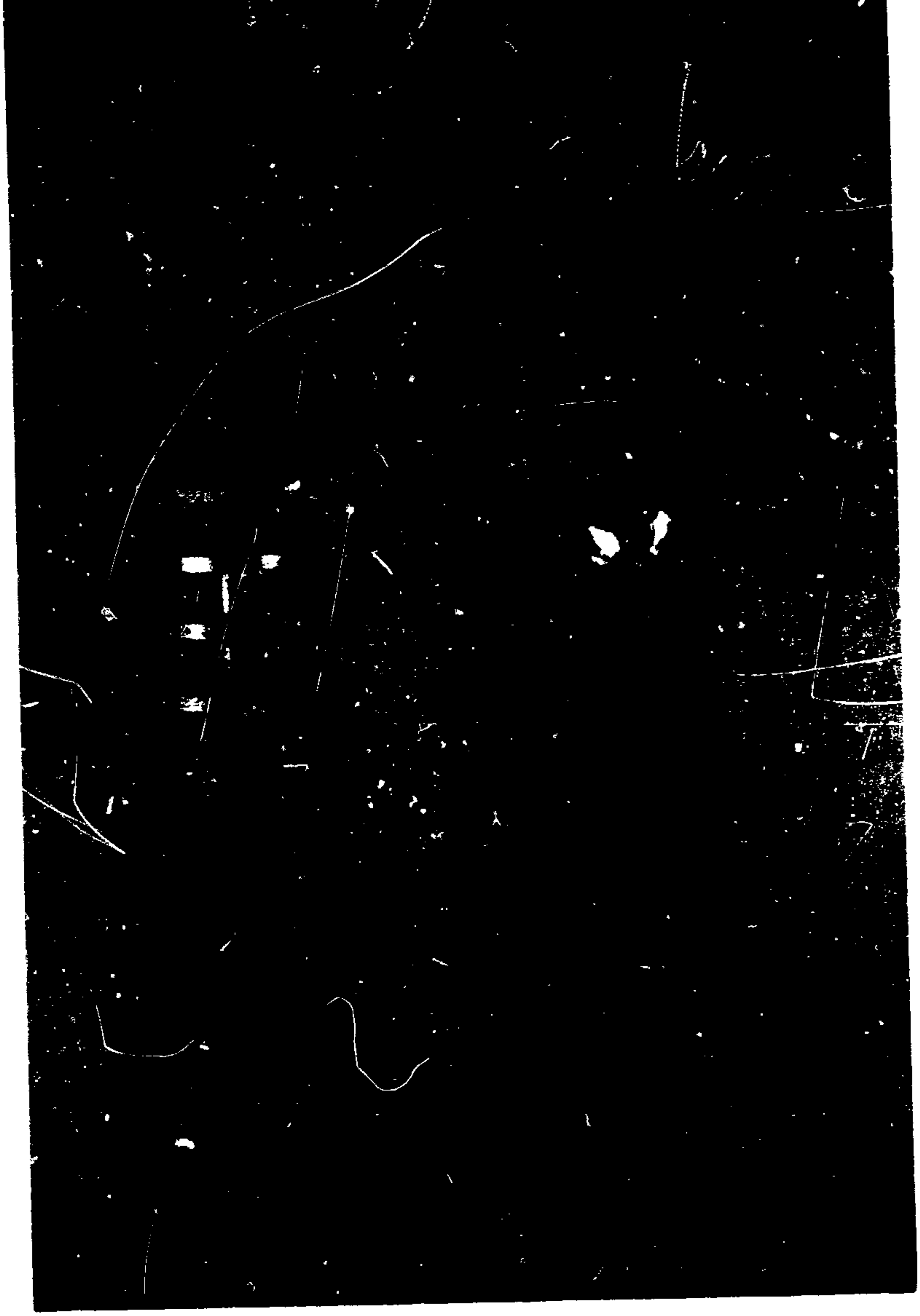

Figure 2. Photograph of Large "Lazy Susan" including Main Deposition Mandrel with Adaptor Ring - Actual Size

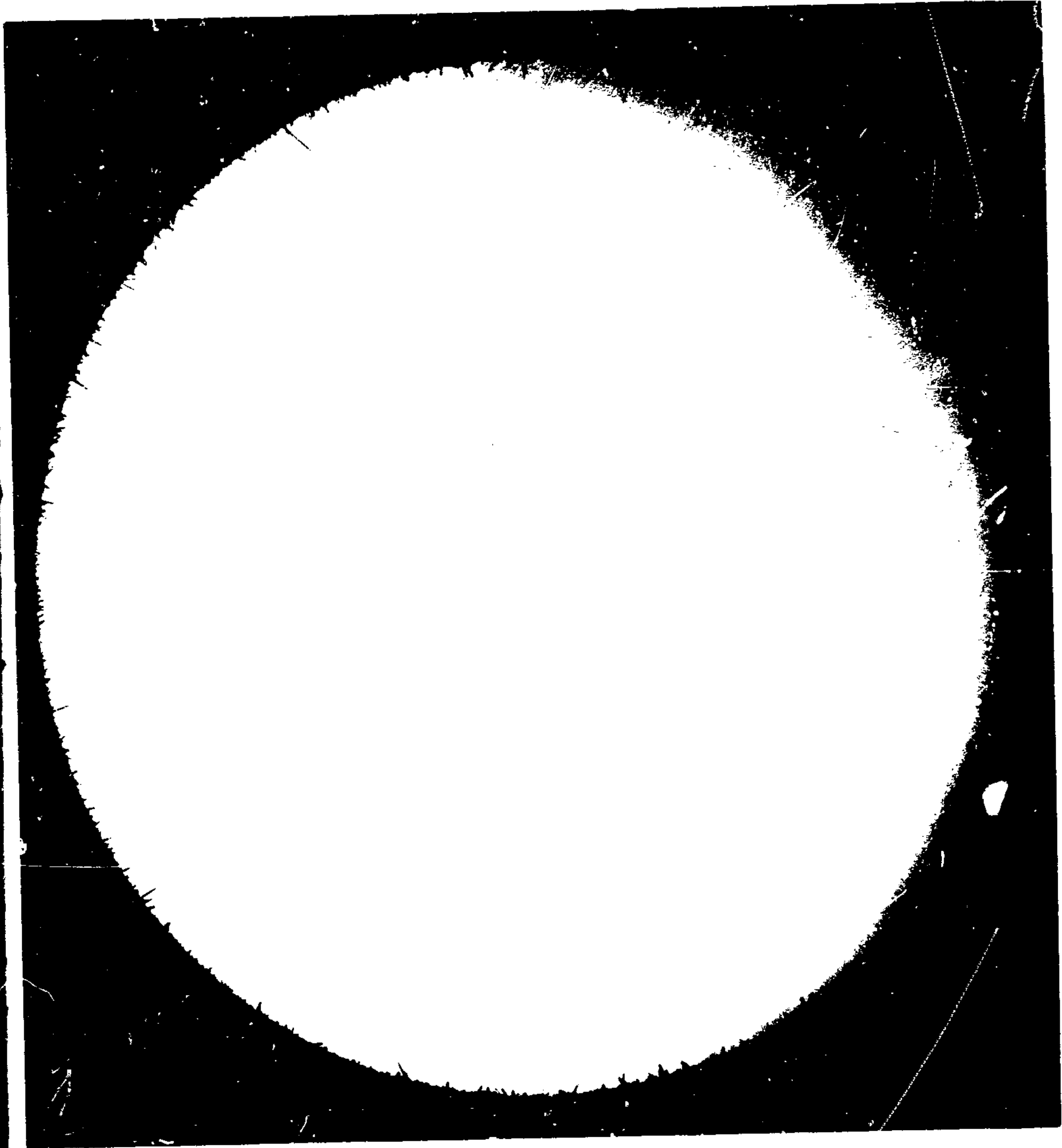

Figure 3. Boron Carbide Whiskers on Deposition Tube Adaptor Ring - 5X

shown in Figure 4, Reference 1) one on top of the other, with a continuous deposition tube extending through both units. This arrangement will allow for the operation of two distinct nine inch temperature zones with a minimum of transition temperature area. Future experiments of both the pure vapor deposition type as well as the dynamic chemical method of gas phase vapor deposition will be pursued. This new furnace design will permit much closer control of temperature and pressure parameters which should directly contribute to the experimental studies.

B. MECHANICAL PROPERTIES OF B_4C WHISKERS

Several preliminary tests have been performed on B_4C whiskers. The apparatus used was a Tecam Micro-Tensile Testing Machine, manufactured by Techne Ltd., Cambridge, England. The machine has been fully described[2]. Briefly, it is a null-balance type machine using a torsion balance to apply loads and a mirror autocollimating telescope system to detect extension. Loads between 1 mgf and 400 gf can be applied, and extensions of about 100Å measured. Specimens can be tested having cross-sections between 10^{-9} mm^2 to $10^{-2} mm^2$ and lengths between 0.5 mm and 15 mm.

The results of the tests performed may be summarized as follows:

Specimen	Length	Area	Ultimate Strength
1	2mm	$292\mu^2$	340,000 psi
2	1.1mm	$\sim 290\mu^2$	190,000 psi

The fracture surfaces appear to be perpendicular to the axis of the specimen and triangular in cross-section. A photomicrograph of specimen 1 after failure is shown in Figure 4. It has not yet been determined, by x-ray diffraction, what the crystallographic orientation is.

Future work will be directed towards obtaining additional data and measuring the elastic modulus. Attempts are being made to grow longer

Figure 4. Fracture Surface of B_4C Specimen No. 1
After Failure - 583X

whiskers, which should greatly facilitate the handling and placement (in the grips) problem.

C. THE CRYSTAL CHARACTER OF B_4C WHISKERS

X-ray diffraction studies of the structure of B_4C whiskers were initiated during this report period. The purpose of this effort was to determine (a) the growth habit(s) of B_4C whiskers and (b) their crystalline perfection. These factors will be correlated with growth conditions and whisker strength. It is hoped that this approach will aid in the optimization of process variables in order that strong whiskers can be produced routinely. Preliminary examination (x-ray) has revealed (a) that not all whiskers are single crystal and (b) that these whiskers may grow with their major axis oriented in at least two different crystallographic directions.

It has been reported in the literature[3] that the system of B_4C is hexagonal with $a_o = 5.61\text{Å}$ and $c_o = 12.07\text{Å}$. Rotation, or layer line, x-ray diffraction photographs were made of the whiskers (in a cylindrical, 57.3 mm diameter, x-ray diffraction camera using Ni filtered copper radiation). The 'average' whisker size was about 0.7mm long with a cross section of about 0.01mm x 0.04mm. A typical layer line x-ray diffraction photograph from a whisker with the predominant growth habit is shown reproduced in Figure 5. The separation between layer lines is related to the repetition distance along the rotation (or major growth) axis of the crystal. In no case was this distance found to be either 5.61Å or 12.07Å. The repetition distance for the whiskers with the predominant growth habit was calculated to be 5.2Å. Therefore it was obvious that the major growth axis in these whiskers was neither parallel to the 'a' nor 'c' crystallographic directions.

Camera Diameter = 57.3mm Copper Radiation, $\lambda = 1.5405\text{A}$

Figure 5. Typical X-ray Layer Line Diffraction Photograph from a B_4C Whisker

It was then observed that the published Miller indices (hkl) for B_4C obeyed the rule that $\frac{1}{3}(-h+k+l)$ = an integer. This indicated that a rhombohedral unit cell could be used to index B_4C. Wyckoff[4] indicates that B_4C can indeed be indexed using a rhombohedral unit in which $a_o = 5.19\text{A}$

and α = 66° 18'. It then appeared that the observed repetition direction (whisker axis) was parallel to the rhombohedral cell edge. None of the photographs exhibited sharp diffraction spots. Instead of sharp spots there were clusters and/or streaks indicating imperfection in the fibers. It appears that individual whiskers of the predominant type contain sections in which the whisker axis is parallel to either the $\frac{1}{3}(-\bar{a}, +\bar{a}_2 + \bar{c})$ or the $\frac{1}{3}(-\bar{a}, -2\bar{a}_2 +\bar{c})$ rhombohedral cell edges.

The above is the result of a preliminary investigation. Later reports will include detailed discussions of the crystal character of B_4C whiskers.

III. CONCLUSIONS

1. Continued improvement in the growth of B_4C whiskers has been accomplished. The length of the whiskers have been increased up to about 50 times that initially attained. This success in turn has enabled strength and structure studies to progress utilizing samples of practical size.

2. Preliminary strength data on a limited number of samples tend to confirm the hypothesis that B_4C whiskers are indeed strong.

3. Structure studies, to date, on B_4C whiskers reveal that whisker axes are not parallel to either of the principal hexagonal unit cell edges ($\bar{a}$ or $\bar{c}$). The whisker axes were found to be parallel to the rhombohedral cell edges, $\frac{1}{3}(-\bar{a}, +\bar{a}_2 +\bar{c})$ and $\frac{1}{3}(-\bar{a}, -2\bar{a}_2 +\bar{c})$.

IV. FUTURE WORK

Growth studies will continue. The re-designed furnace, capable of accurate and separate temperature adjustments of vaporizing areas and the deposition areas should lead to further improvements in the size and number and quality of B_4C whiskers. Also the effects of impurities will be more easily studied. The dynamic flow method previously described which had been temporarily discontinued, will now be fully and finally evaluated.

Mechanical property studies will increase since this phase is essential to the future of the program. Mechanical property studies of B_4C whiskers will continue and expand in order to determine their nature and to estimate the future usefulness of such materials.

Structure studies will continue along with the strength studies so that important variables such as orientation and growth types can be integrated into the accumulated strength data. Also basic information on the B_4C crystal structure will be determined.

Preliminary studies concerned with the utilization of B_4C whiskers in composites will include the following:

1. Choice of a suitable metallic matrix.
2. Coating, wetting and bonding studies of B_4C whiskers.

ACKNOWLEDGEMENTS

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REFERENCES

1. A. Gatti, R. Cree and E. Feingold, "The Synthesis of Boron Carbide Filaments." First Quarterly Report for NASA Contract NASw-670.

2. D. M. March, "Micro-Tensile Testing Machine." J. Sc. Inst. 38, June 1961, 229-234.

3. R. D. Allen, J. Am. Chem. Soc., 75, 3582 (1953).

4. R. W. G. Wyckoff, Crystal Structures, Volume II.